ORDINARY GASEOUS DIFFUSION

BY

DUDLEY DAVIS KIMPTON

B.S., Case School of Applied Science, 1945
M.S., Case School of Applied Science, 1946

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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Introduction

Accurately determined values of the diffusion constants of gases are of interest for several reasons. First, they serve as an indication of how rapidly mixing by the diffusion process will occur. Second, it is possible by the use of theoretical results obtained by Chapman and Cowling[1a] to calculate the mean molecular diameter of a gas pair from the diffusion coefficient. This calculation gives information related to the van der Waals dimensions and leads to some insight regarding the force fields between molecules. From a more practical standpoint diffusion data is of great value in the designing of columns for the thermal separation of isotopes.

In this investigation the diffusion constant of water vapor into air was checked and the diffusion constants for water vapor - methane, water vapor - ethane, water vapor - ethylene, water vapor - propane, water vapor - sulfur dioxide, and heavy water vapor - air were determined for the first time. Also the temperature dependence of the diffusion coefficient was investigated for the systems heavy water vapor - air and water - methane.

Theory

When a gas contains two or more different kinds of molecules whose relative densities vary from point to point, a process called diffusion is observed to occur in such a way as continually to diminish the inequalities of composition. The net flow of each kind of molecule will obviously occur in the direction of its negative density gradient, i.e., in the direction in which the density decreases most rapidly.

Let us consider a mixture of two gases confined to a cylindrical tube parallel to the x direction, and let us assume that the composion is a function only of x and of the time, t. If n_1 and n_2 are the number concentrations of the two gases,

then the net number of a given kind of molecule crossing a unit area perpendicular to the x direction will in unit time be equal to

$$r_1 = - D_{12} \frac{dn_1}{dx} \quad ; \quad r_2 = - D_{12} \frac{dn_2}{dx}$$

where D_{12} is the coefficient of mutual diffusion.

According to the mathematical theory of non-uniform gases[1a] a first approximation to the coefficient of mutual diffusion is given by

$$D_{12} = \frac{3}{8n\sigma^2_{12}} \left\{ \frac{kT(m_1 + m_2)}{2\Pi m_1 m_2} \right\}^{1/2}$$

Equation (1) was derived on the assumption that the molecules are rigid elastic spheres of masses m_1 and m_2 with diameters σ_1 and σ_2. The mean diameter, $\sigma_1 + \sigma_2 / 2$ is defined as σ_{12} and the total concentration $n_1 + n_2$, is denoted by n. Higher approximations show that D_{12} depends to some extent upon the composition of the gas mixture, but this dependence is very slight and is usually neglected.

Experimental

The experimental procedure used was that devised and developed by Stefan.[2] One of the two components in the liquid state was placed in a small glass tube, filling the tube within 1 to 5 cm. of the top. The tube and liquid were held at constant temperature, and the second gas was passed over the top of the tube. The diffusion coefficient was then calculated from the rate of evaporation of the liquid by use of the ordinarilly integrated form of Stefan's diffusion equation. All diffusion coefficients are in cm^2/sec and are reduced to a pressure of 760 mm Hg.

Results and Conclusions

Table I gives a summary of the results obtained in this

investigation.

TABLE I

SUMMARY OF RESULTS

Gas Pair	Temp. (°C)	D_{12} (cm^2/sec)	σ_{12} (A)
H_2O - air	24.8	0.257	3.32
H_2O - CH_4	24.8	0.251	3.60
H_2O - CH_4	40	0.278	3.55
H_2O - CH_4	50	0.297	3.52
H_2O - CH_4	60	0.313	3.50
H_2O - C_2H_6	24.8	0.177	3.99
H_2O - C_2H_4	24.8	0.178	4.01
H_2O - C_3H_8	24.8	0.156	4.12
H_2O - SO_2	24.8	0.124	4.51
D_2O - air	24.8	0.237	3.41
D_2O - air	40	0.277	3.27
D_2O - air	45	0.288	3.25
D_2O - air	60	0.314	3.22

The value of 0.257 found for H_2O - air at 24.8°C is in good agreement with the value of 0.258 found by Gilliland.[3]

The mean molecular diameters of H_2O and the various hydrocarbons show an increase as the molecular weight of the hydrocarbons increases. This is the result which would be expected. However a discrepency appears in the result for H_2O - C_2H_6 as compared to H_2O - C_2H_4, since C_2H_4 is known to have the smaller molecular diameter. This may be due to the fact that the C_2H_6 used was only 95% pure, while all the other hydrocarbons employed were of 99% purity. If the impurity in the C_2H_6 consisted largely of lower molecular weight materials such as H_2 and CH_4, the low result obtained would be expected.

It is interesting to note that a mass effect alone is not sufficient to account for the difference in the diffusion coefficients of H_2O - air and D_2O - air. The mean molecular diameter of H_2O - air at 24.8°C was calculated to be 3.32 A and that of D_2O - air 3.41 A. This is in qualitative agreement

with results obtained by viscosity measurements reported by Chapman and Cowling.[1b] They give the molecular diameter of H_2 as 2.63 A and that of D_2 as 2.76 A, and hence D_2O would be expected to have a slightly higher molecular diameter than H_2O.

The diffusion coefficients for the system H_2O - CH_4 appeared to be proportional to T^2 for the four temperatures investigated. For the system D_2O - air no proportionality could be established between the diffusion constant and a power of the temperature. The values obtained for the diffusion constant at 24.8°C, 40°C, and 45°C are nearly proportional to T^3, but the value obtained at 60°C is much less than this proportionality would predict. The peculiar behavior of the system D_2O - air may be due in part to the fact that D_2O tends to exchange with the water vapor in the atmosphere. Hence the determinations involving D_2O are somewhat less reliable than those involving ordinary water.

For both H_2O - CH_4 and D_2O - air the value of the mean molecular diameter decreased with increasing temperature. This is to be expected since as the temperature increases the kinetic energy increases and hence the distance of closest approach decreases.

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VITA

The author was born in Akron, Ohio on February 15, 1924. He attended the elementary schools of Bath and Stow Townships and in 1942 graduated from Stow High School. In the Fall of 1942 he entered Case School of Applied Science at Cleveland, Ohio. He received the B.S. degree from Case in April 1945, and the M.S. degree from the same institution in January 1947. While studying for the M.S. degree he was employed as a special research assistant for the Lubrizol Corporation of Cleveland. In the Fall of 1946 he entered the Graduate School of the University of Illinois. He has been a graduate assistant on the staff in physical chemistry since that time. He is a member of Sigma Xi, Alpha Chi Sigma, and the American Chemical Society.

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